3 POTENTIALLY CONTROLLABLE METHYLATION PROCESSES IN THE DELTA

The problem with mercury in the Delta's aquatic ecosystems can be defined as biotic exposure to methylmercury (Wiener *et al.*, 2003a). Therefore, decreasing biotic exposure to methylmercury is the ultimate goal of the Delta methylmercury TMDL and implementation program. Several published papers provide comprehensive reviews of the current knowledge of the methylmercury cycle (e.g., Wiener *et al.*, 2003a & 2003b; Tetra Tech, Inc. 2005; LWA, 2002). This chapter focuses on the processes that are potentially controllable in the Delta. The concepts summarized in this chapter guided the development of the methylmercury TMDL for the Delta, particularly the linkage analyses (Chapter 5), methyl and total mercury source analyses (Chapters 6 & 7), and recommended methylmercury allocations and total mercury limits (Chapters 8). Data gaps and uncertainties associated with each factor are identified in this chapter and then addressed further by recommendations for source characterization and control studies in Chapter 4 of the Proposed Basin Plan Amendment draft staff report.

Methylmercury concentrations in aquatic ecosystems are the result of two competing processes: methylation and demethylation. Neither is well understood. Methylation is the addition of a methyl group to an inorganic mercury molecule (Hg^{+2}). Sulfate reducing bacteria are the primary agents responsible for the methylation of mercury in aquatic ecosystems (Compeau and Bartha, 1985; Gilmour *et al.* 1992). Small amounts of methylmercury also may be produced abiotically in sediment (Falter and Wilken, 1998). Maximum methylmercury production occurs at the oxic-anoxic boundary in sediment, usually several centimeters below the surface. Although less common, methylmercury also may be formed in anaerobic water (Regnell *et al.*, 1996 & 2001). In this case, mercury-methylating microbes move from the sediment to the overlying water and the resulting methylmercury becomes available to the biotic community when aerobic and anaerobic waters mix.

Demethylation is both a biotic and abiotic process. Both sulfate reducing and methanogen-type bacteria have been reported to demethylate mercury in sediment with maximum demethylation co-occurring in the same zone where maximum methylmercury production is located (Marvin-DiPasquale *et al.*, 2000). Photodegradation of methylmercury in the water column also has been observed (Sellers *et al.*, 1996; Byington *et al.*, 2005). While not well studied, the rate of both biotic and abiotic demethylation appear quantitatively important in controlling net methylmercury concentrations in aquatic ecosystems (Sellers & Kelly, 2001; Marvin-DiPasquale *et al.*, 2000).

Factors controlling sediment methylmercury production have been the subject of intense scientific research (for reviews see Wiener *et al.*, 2003b and Benoit *et al.*, 2002). Sediment factors and landscape events important in net methylmercury production include:

- Sulfate and pH concentration of the overlying water (Gilmour *et al.*, 1998; Miskimmin *et al.*, 1992; Krabbenhoft *et al.*, 1999);
- Percent organic content of the sediment (Krabbenhoft *et al.*, 1999; Miskimmin *et al.*, 1992; Hurley *et al.*, 1998; Heim *et al.*, 2003; Slotton *et al.*, 2003);
- Creation of new water impoundments (Verdon *et al.*, 1991; Bodaly *et al.*, 1997);
- Amount and kind of inorganic mercury present in the sediment (Krabbenhoft *et al.*, 1999; Bloom, 2003); and

- Amount of permanent or seasonally flooded wetland in a watershed (Krabbenhoft *et al*., 1999; Brumbaugh *et al*., 2001; St Louis *et al*., 1994 & 1996; Hurley *et al*., 1995).

The organic content of the sediment and the pH of the overlying water are not discussed further as neither appears controllable in the Delta.

3.1 Sulfate

Sulfate is used by sulfate reducing bacteria as the terminal electron acceptor in the oxidation of organic material. Sulfate additions have been observed to both stimulate (Gilmour *et al.*, 1992; King *et al.*, 2002) and inhibit (Benoit *et al.*, 1999; Gilmour *et al.*, 1998) methylmercury production. Addition of sulfate is predicted to stimulate methylmercury production when it is limiting. In contrast, sulfate amendments may inhibit production when excess sulfide is present. Sulfide is the primary byproduct in the reduction of sulfate and increasing sulfide concentrations may cause inhibition by either decreasing the amount of neutrally charged dissolved mercury-sulfide complexes[8] (Benoit *et al.*, 1999 & 2001, but see Kelley *et al.*, 2003, for conflicting results) or by precipitating insoluble mercuric sulfide (Compeau & Bartha, 1985).

Two factors influencing sulfate concentrations in the Delta-Estuary are the Water Quality Objectives for electrical conductivity (EC) and the ratio of San Joaquin River to Sacramento River water. Both are controllable water quality factors and result from water management decisions made by the State of California. Table 3 of Water Rights Decision 95-1WR stipulates maximum ambient electrical conductivity values for various locations in the Delta by month and water year type (SWRCB, 1995). Electrical conductivity in the estuary is primarily a function of freshwater outflow and seawater intrusion.[9] Water Right Decision 95-1WR regulates electrical conductivity by specifying both the amount of freshwater outflow and the amount of water exported to Southern California. For example, during 2000-2001, the 2 o/oo salinity level[10] in ambient bottom water was located as far seaward as the City of Martinez in March 2000, but migrated as far upstream as Rio Vista in the summer of 2001 (Foe, 2003). The upstream movement of the salinity field had the effect of increasing sulfate concentrations in western Delta water by about ten-fold.

Sulfate concentrations are about seven times higher in the San Joaquin River than in the Sacramento River. At present, the San Joaquin River is almost entirely diverted out of the Delta by way of Old River and Grantline Canal for export to southern California via the State and Federal Pumping facilities near Tracy. This reduces the proportion of San Joaquin River water in much of the southern and central Delta and allows intrusion of Sacramento River water with lower sulfate concentrations. The Record of Decision for the CALFED Bay-Delta Program committed the State to evaluate and, if practical, begin construction of a series of permanent, operable barriers in the southern Delta to better control the routing of San Joaquin River water (CALFED Bay-Delta Program, 2004B). An indirect consequence of the permanent barriers is that their operation will determine sulfate concentrations in much of the central and southern Delta.

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[8] Dissolved, neutrally charged mercury is the only form that readily crosses microbial cell membranes.

[9] Sulfate concentrations in the Sacramento and San Joaquin Rivers varied between 6-14 and 42-108 mg/l in 2000 and 2001 (Foe, 2003) while full strength seawater is 2,700 mg/l (Parsons and Takahashi, 1975).

[10] Salinity is generally reported in terms of parts per thousand (abbreviated o/oo), the number of pounds of salt per 1,000 pounds of water.

Sulfate amendment studies need to be undertaken with sediment collected throughout the year from the southern, central and western Delta to determine whether the sulfate concentration in the overlying water affect methylmercury production in sediment. Results of these experiments can be considered when evaluating how to manage the permanent, operable barriers in the southern Delta and when considering water right decisions to modify the location of the salinity field in the estuary.

3.2 New Water Impoundments

The creation of new water impoundments has been found to stimulate sediment microbial activity and to increase methylmercury concentrations in sediment, water and biota (Verdon *et al.*, 1991; Bodaly *et al.*, 1997). The State of California has a growing population and a limited water supply for municipal and agricultural use. One alternative under evaluation is the construction of additional reservoir storage. The Record of Decision for the CALFED Bay-Delta Program directs agencies and local interests to continue to evaluate five surface water storage options to improve water management (CALFED Bay-Delta Program, 2004A). These include north of Delta off-stream storage, in-Delta storage, Shasta Lake expansion, Los Vaqueros Reservoir expansion and upper San Joaquin storage. Environmental planning for each project is underway and should evaluate the potential of each new facility to increase downstream methylmercury concentrations in the Delta.

3.3 Sediment Mercury Concentrations

Methylmercury production has been found to be a function of the total mercury content of the sediment. Methylmercury concentrations[11] adjusted for the organic content of the sediment increased logarithmically with increasing total mercury concentration in a study of 106 sites from 21 basins across the United States (Krabbenhoft *et al.*, 1999). The slope of the relationship was linear to approximately 1 mg/kg total mercury before commencing to asymptote. Similar linear relationships have been observed in the Delta between methyl and total mercury concentrations in sediment (Table 3.1). The statistical significance of the correlation increases when data from one land use type (e.g., marshes) are used. This implies that methylation rates may also be a function of habitat type. The results are consistent with laboratory experiments where increasing concentrations of inorganic mercury were amended into sediment and the evolution of methylmercury monitored. The efficiency of the conversion of total to methylmercury was linear to about 1 mg/kg before commencing to level off (Bloom, 2003; Rudd *et al.*, 1983).

[11] Radiotracer experiments in Florida Everglade sediment demonstrate that methylmercury production is positively correlated with bulk sediment methylmercury concentrations (Gilmour *et al.*, 1998). Moreover, the spatial pattern of methylmercury production was strongly correlated with aqueous and biotic concentrations, suggesting that surficial sediment concentrations could be used as an analog for *in situ* methylmercury production and flux into the overlying water. Bulk methylmercury sediment concentrations are now widely used as an index of methylmercury production (Krabbenhoft *et al.*, 1999; Bloom *et al.*, 1999 and 2003; Heim *et al.*, 2002; Slotton *et al.*, 2002; Conaway *et al.*, 2003; Benoit *et al.*, 1999).

Table 3.1: Field Studies Demonstrating a Positive Correlation Between Total and Methylmercury in Freshwater Surficial Sediment

Location (a)	R^2	**P-Value**	**Comments**	**Author**
Sacramento-San Joaquin Delta Estuary	0.2	<0.01	All habitats in Delta combined.	Heim *et al.*, 2003
Sacramento-San Joaquin Delta Estuary	0.52	<0.001	Only marsh habitats.	Heim *et al.*, 2003
Sacramento-San Joaquin Delta Estuary	0.37	<0.001	Comparisons inside and outside of flooded Delta Islands.	Slotton *et al.*, 2003
Elbe River	0.69	<0.0001	Germany.	Hintelmann & Wilken, 1995
Patuxent River Estuary	0.61	<0.05	Sub embayment of Chesapeake Bay.	Benoit *et al.*, 1998
National Survey	0.62	<0.0001	Log/log relationship normalized to percent organic carbon at 106 sites in 21 basins across the United States.	Krabbenhoft *et al.*, 1999
Lake Levrasjon	0.64	<0.05	Southern Sweden.	Regnell *et al.*, 1997

(a) The majority of the sediment in each study had a mercury content less than 1 ppm.

Mercury concentrations in fish at contaminated sites decline after control measures are instituted to reduce incoming mercury loads (Table 3.2). Most sites studied to date are industrial facilities that discharge to fresh water and have operated for relatively short periods.[12] The initial decrease in fish tissue concentration near the source of contamination is often fast with about a 50% decline in the first five to ten years. However, after a rapid initial decrease, concentrations tend to stabilize with little, if any, subsequent decline (Turner & Southworth, 1999; Takizawa, 2000; Lodenius, 1991; Lindestrom, 2001; Francesconi *et al*., 1997). The new equilibrium value is usually higher than in adjoining uncontaminated waterways and is also often greater than what is recommended as safe for human consumption (Turner & Southworth, 1999; Parks & Hamilton, 1987; Lodenius, 1991; Lindestrom, 2001; Francesconi *et al*., 1997; Becker & Bigham, 1995). The reasons are unclear but may be because small amounts of mercury are still entering from terrestrial sources (Turner and Southworth, 1999) or because of difficulties in bringing sediment concentrations down to background levels (Francesconi *et al*., 1997; Jernelov & Asell, 1975). If contamination has spread to areas more distant than the immediate facility, then reductions in fish tissue concentrations are much slower (Southworth *et al*., 2000). Absent from the literature are reports on remediation of pollution from mercury mining. The magnitude and duration of mercury and gold mining in California, coupled with the extensive distribution of contamination, will likely make recovery much slower than at industrial sites (Table 3.2).

As part of the mercury control program for San Francisco Bay, San Francisco Water Board staff established a goal for Bay sediment of 0.2 mg/kg mercury and assigned Central Valley outflows a total mercury load reduction of 110 kg per year to achieve it (Johnson & Looker, 2004). Waterborne mercury and total suspended sediment loads in the Delta's tributaries are summarized in Chapter 7. Initial

[12] One to two decades.

Table 3.2: Change in Fish Tissue Mercury Concentration After Initiation of Source Control.

Location	Mercury Source	Biotic Change	Control Measures	References
Oak Ridge National Laboratory, Tennessee	Weapons Facility	Sunfish at discharge point declined from 2 to 1 mg/kg in 5 yrs; half mile downstream sunfish declined from 0.9 to 0.7 mg/kg in 9 yrs; no change in tissue 2 and 5 miles downstream.	Reduced discharge, excavated portion of flood plain.	Turner & Southworth, 1999; Southworth *et al*., 2000
Lake St. Clair, Michigan	Two Chloralkali Plants	Walleye fish declined from 2.3 to 0.5 mg/kg in 25 yrs	Reduced/eliminated discharge	Turner & Southworth, 1999.
Abbotts Creek, North Carolina	Battery Manufacturing plant	Fish declined from 1 to 0.5 mg/kg in 11 yrs	Treated groundwater, reduced/eliminated discharge, removed contaminated soil, natural sediment burial	Turner & Southworth, 1999
Saltville, Virginia	Chloralkali Plant	Rockfish declined from 3.5 to 1 mg/kg in 20 yrs	River sediment dredged, rock bottom grouted, rip-rap river bank, pond seepage treated with activated carbon	Turner & Southworth, 1999
Howe Sound, British Columbia, Canada	Chloralkali Plant	Dungeness crab declined from 2 to 0.2 mg/kg in 5 yrs. No subsequent change	Reduced/eliminated discharge, treated groundwater	Turner & Southworth. 1999
Little Rock Lake, Wisconsin	Atmospheric deposition	Yellow Perch declined 30% in 6 yrs	Reduced atmospheric mercury input by 60%.	Hrabik & Watras, 2002.
Minimata, Japan	Chloralkali Plant	Fish declined from 9.0 to 0.4 mg/kg in 8 yrs; no further change.	Eliminated discharge; dredged and disposed of sediment.	Takizawa, 2000
Clay Lake, Ontario, Canada	A chloralkali plant and a wood pulp mill.	Walleye fish declined from 15.1 to 2.0 mg/kg in 20 yrs. Background concentration is 0.6 mg/kg.	Eliminated discharge; natural burial of contaminated sediment	Parks & Hamilton, 1987; Turner & Southworth, 1999.
Ball Lake, Ontario, Canada (downstream of Clay Lake)	Same as above	Walleye fish declined from 2.0 to 1.4 mg/kg in first 5 yrs. Northern Pike from 5.1 to 1.8 mg/kg. No change in Lake Whitefish.	Same as above	Armstrong & Scott, 1979
Lake Kirkkojarvi, Finland	Phenylmercury in slimicide in pulp mill	4 and 1-kg Northern Pike declined from 3.6 to 2.1 and from 1.5 to 0.8 mg/kg in 20 yrs. All reductions happened in first 10 yrs. Background concentration in 1-kg pike is 0.4 mg/kg.	Reduced discharge, natural burial	Lodenius, 1991
Lake Vanern, Sweden	Chloralkali Plant	5-yr old Northern Pike declined from 1.4 to 0.6 mg/kg in 25 yrs. Most of decrease occurred in first 10-15 yrs. Background concentrations in Pike are 0.4 mg/kg	Reduced/eliminated discharge, natural burial	Lindestrom, 2001
Princess Royal Harbor, Australia (Marine water)	Superphosphate Processing Plant	Mercury in 8 marine fish species declined by about 50% in 9-yrs. Most of decrease happened in first 4-yrs. Tissue concentrations are still about twice background.	Eliminated discharge, natural burial	Francesconi *et al*., 1997
Onondaga Lake, New York	Municipal and industrial discharge	Mercury in six fish species declined by 60 to 80 % in 22 yrs. Tissue concentrations are still about twice background.	Eliminated discharge, natural burial	Becker & Bigham, 1995.
North Carolina, Quebec, Finland, Manitoba, Labrador and Newfoundland	Reservoir creation	Fish tissue levels declined to normal after 3 to 30 years.	None	As reviewed in French *et al.*, 1998.

management actions of the Delta mercury TMDL could consider controlling mercury from watersheds with high methylmercury concentrations in fish, high mercury to suspended sediment ratios and large areas of downstream marsh. The initial goal would be to meet the San Francisco Water Board's goal of 110 kg total mercury reduction per year, but additional load reductions eventually may be needed to achieve compliance with the Central Valley Water Board's proposed fish tissue targets for the Delta (Chapter 4).

3.4 Forms of Mercury

Two different forms of mercury are transported into the Delta with potentially different methylation rates. The first form is mercury mine waste from the Coast Range. Most of this material is thought to be mercuric sulfide, cinnabar and metacinnabar (Bloom, 2003). Mercury mine waste enters the Delta from mine-impacted coast range creeks such as Putah and Cache Creeks. The second form is elemental mercury lost from placer gold mining operations in the Sierra Nevada Mountains. Elemental mercury enters the Delta in Sacramento, Mokelumne and San Joaquin River water that drains from the northern and southern gold fields.

Mercury from gold mining appears to be more biologically available than material from mercury mines. The evidence is twofold. First, Frontier Geosciences conducted a 1-year microcosm incubation study with both gold and mercury mine waste to determine the relative methylation efficiency of each (Bloom, 2003). Mercury from gold mining was found to have the higher methylation rate. Second, the ratio of methyl to total mercury in natural sediment is assumed to be a field measure of methylation efficiency (Gilmour *et al.*, 1998; Krabbenhoft *et al.*, 1999; Bloom *et al.*, 1999 and 2003). Heim and others (2003) collected sediment at multiple locations in Cache Creek (representative of mercury mine waste) and the Cosumnes River (representative of gold mine material) on three occasions (October 1999, May 2001 and October 2001) to determine methyl and total mercury concentrations and methylation efficiencies. The highest methyl to total mercury ratios were consistently observed in Cosumnes River material. These results are consistent with the conclusions of Bloom (2003) and suggest that floured elemental mercury from gold mining in the Sierra Nevada is more readily methylated than is cinnabar from the Coast Range.

Heim and others (2003) also collected sediment samples at multiple locations in Cache Creek. The ratio of methylmercury to total mercury increased with increasing distance from the mercury mining districts. The authors speculate that diagenic weathering-type processes are changing the form of the mercury and increasing its methylation efficiency as the material is slowly transported away from the mines. The precise mechanisms are not known but may include the formation of soluble polysulfide complexes (Paquette & Heltz, 1995) and dissolution of cinnabar by humic and fulvic acids (Wallschlaeger *et al.*, 1998; Ravichandran *et al.* 1998). Both processes should increase the efficiency of the conversion of inorganic to organic mercury. No similar weathering type experiments have been conducted on Sierra Nevada gold mine-derived mercury. The Cache Creek findings suggest that there is currently insufficient understanding of mercury weathering processes to justify developing control programs that preferentially target controlling gold-mine waste material.

3.5 Wetlands

Research in the Delta and elsewhere has found that wetlands are sites of efficient methylmercury production (Slotton *et al.*, 2003; Heim *et al.*, 2003; St. Louis *et al.*, 1994, 1996; Gilmour *et al.*, 1998). In fact, one of the best predictors of methylmercury concentrations in water and in biota is the amount of wetland present in upstream watersheds (Krabbenhoft *et al.*, 1999; Wiener *et al.*, 2002). The Record of Decision for the CALFED Bay-Delta Program commits the Authority to restore 30,000 to 45,000 acres of fresh, emergent tidal wetlands in the Delta by 2030 (CALFED Bay-Delta Program, 2000a). Many of the proposed sites are downstream of mercury-enriched watersheds. Marsh restoration efforts below mercury enriched watersheds are proposed for the following locations: Yolo Bypass downstream of Cache and Putah Creeks; Dutch Flats downstream of the Mount Diablo Mercury mine in the Marsh Creek watershed; and Staten Island and the Cosumnes River Wildlife Refuge near the confluence of the Cosumnes River and Mokelumne River. Extensive restoration efforts in the Delta have the potential to increase methylmercury exposure for people and wildlife.

Key Points

- The problem with mercury in the Delta's aquatic ecosystems can be defined as biotic exposure to methylmercury. Therefore, decreasing biotic exposure to methylmercury is the ultimate goal of the Delta methylmercury TMDL and implementation program.
- The implementation plan could focus on sources and processes that are potentially controllable in the Delta. Potentially controllable sediment factors and landscape events important in net methylmercury production include: water rights salt standards in the Delta; creation of new water impoundments; amount of inorganic mercury present in the sediment; and amount of permanent or seasonally flooded wetland in a watershed.